Section 8

NEW DIRECTIONS FOR REFORMULATING ALCOHOL FUELS TO OVERCOME OPERATIONAL PROBLEMS

Quick Reference Data

Cetane Numbers

Diesel	=	45 to 55
Ethanol	=	8
Methanol	=	3

Electric Conductivity

(mbo/cm)	
Gasoline	1×10^{-14}
Diesel Fuel	1×10^{-12}
Ethanol	1.35×10^{-9}
Methanol	4.4×10^{-7}

Viscosity

	Centipoise	
	20°C	-20°C
Methanol	0.59	1.15
Ethanol	1.19	2.84
Diesel Fuel	9.7	1.15

Useful Terms and Definitions (also see Glossary)

- **Cetane Number (Rating)**: a measure of the ignition value of a diesel fuel (i.e., the percentage by volume of the hydrocarbon cetane ($C_{16}H_{34}$) in a mixture of cetane and 1-methylnaphthalene that gives the same ignition lag as the fuel oil being tested).

Issues and Implications:

Issue #1: Low Cetane Numbers of Fuel Alcohols

Neat alcohol fuels will not self-ignite in existing compression ignition (diesel) engines.

Implications of Low Cetane Numbers:

- Alcohols cannot be used in existing diesel engines to replace diesel fuel without modifying the engine or adding supplemental additives.

Proposed Solutions:

- The use of additives in alcohol fuels currently appear to be much more promising than modifying the diesel engine (such as using continuously operating glow plugs). "Ignition improver" additives that have shown significant success include peroxides, nitro-compounds (Avocet™), nitrocellulose, or nitrates. For example, the addition of 7.5% Avocet™ to methanol has resulted in similar combustion characteristics to diesel fuel when burned in a diesel engine.

Detailed Information: Refer to pages 8-2 through 8-4.

Issue #2: Phase Separation of Alcohol/Gasoline Blends

Implications of Phase Separation:

- Loss of cold weather driveability
- Potential fuel line freezing

Proposed Solutions:

- In addition to improved alcohol storage and shipping techniques to prevent water contamination, gasoline/alcohol blends can be reformulated to avoid phase separation by introducing additives such as "higher" alcohols, various nonionic surfactants, and various anionic fatty acid surfactants.

Detailed Information: Refer to pages 5-7 through 5-10 and 8-4.

Issue #3: Electrical Conductivity

The comparatively high electrical conductivity and high oxygen content of fuel alcohols can contribute to corrosion and wear problems as well as chemical degradation of materials in a vehicle's fuel system.

Implications of High Conductivity of Alcohol Fuels:

Current flows from rear-mounted fuel pumps can induce galvanic corrosion.

Proposed Solutions:

- Selecting materials compatible with the properties of alcohols will help alleviate these problems.

- Using corrosion inhibitor additives and higher alcohols (such as 1-butanol or n-decanol) as cosolvents with fuel alcohols inhibits corrosion of water-sensitive materials such as aluminum.

Detailed Information: Refer to pages 7-4 through 7-5 and 8-5.

Issue #4: Viscosity

Ethanol and methanol have low viscosity which may lead to lubrication problems, especially in diesel fuel engines modified to run on alcohol fuels.

Implications of Low Viscosity:

Increased wear due to less effective lubrication.

Proposed Solution:

- Use of higher alcohols as additives may be needed to improve lubricity.

Detailed Information: Refer to pages 8-6.

Issue #5: Cold Weather Starts

Neat alcohol-fueled engines have proven difficult to cold start, especially at ambient temperatures below 10°C (50°F).

Implication of Cold Weather Starting Problems:

- Prolonged engine cranking
- Battery wear

Proposed Solutions:

- Neat alcohols will require either "reformulated" mixtures using some form of additive (such as gasoline, dimethyl ether (DME)), or some other cold start subsystem.

Detailed Information: Refer to pages 8-6.

Section 8
NEW DIRECTIONS FOR REFORMULATING ALCOHOL FUELS TO OVERCOME OPERATIONAL PROBLEMS

- Cetane Number
- Miscibility with Water and Hydrocarbon Fuels
- Electric Conductivity and Oxygen Content
- Viscosity
- Material Compatibility
- Safety Issues
- Cold Startability

Introduction

Ethanol and methanol have many important properties that make them quite different from gasoline and diesel fuel (see Table 2-4). **Modifications to certain properties of ethanol and methanol would improve their performance as alternative liquid transportation fuels.** Therefore, this section will focus on opportunities to modify specific properties of alcohol fuels to improve engine/vehicle performance. A number of technical alternatives are feasible. At the two extremes, one can either blend in one or more additives to the ethanol or methanol to improve its characteristics, or redesign the engine to take full advantage of the alcohol fuel's properties. Because of the cost and complexities involved in new engine design, most recent efforts and fleet tests have tended to modify an existing diesel/gasoline engine, test the use of an additive in the fuel, or both. In this section, the focus is exclusively on reformulations of the basic alcohol fuel, primarily through the addition of higher alcohols, to lessen or eliminate existing operational problems.

A set of requirements must be established for the properties of any additive. The additive must be physically and chemically compatible with the base alcohol fuel and have preferably have the same or higher specific energy content. Additives must not be readily removable from the fuel, significantly add to exhaust emissions, nor leave any residue. Moreover, additives should not complicate regulatory compliance, and should also be relatively inexpensive.

Cetane Number

Policy Issue #1

> Diesel engines use compression and heat to auto-ignite the fuel. The cetane number is a measure of the ignition value of diesel fuel. Most diesel fuel has a cetane numbers ranging from 45 to 55. The "low" cetane number of ethanol (8) and methanol (3) indicates an insufficient self-ignition quality for direct use of these alcohols in unmodified diesel engines.

Additives must be used with alcohol fuel to improve its self-ignition properties. [1,2] These additives are called "ignition improvers."

Figure 8-1 [3] shows the influence of the fuel's cetane number on the concentration required of the ignition improver to obtain the same ignition delay as a conventional diesel fuel (cetane number 52). Peroxides and nitro-compounds such as Avocet™ and nitrocellulose are suitable ignition improving additives for poor quality diesel fuels and for middle distillate fuels. In Sweden, 2% Avocet™ is also being tested as an additive to allow lignocellulosic ethanol to be used as a primary fuel in diesel buses. [4] Nitrates are also valuable additives for low cetane number fuels such as alcohols. Such additives can boost the performance of normally low cetane number fuels such as ethanol and methanol to those of commercial diesel fuels. For example, tests were made with methanol plus an ignition-improving additive consisting of a modified nitrocellulose (NC) combined with polyether to avoid solid deposits in the injection system. In comparison with conventional diesel operation, the combustion of the methanol plus the ignition improver exhibits nearly equal fuel consumption and ignition and ignition delay behavior. The enhanced methanol blend demonstrated much lower NO_x, soot, and particulate emissions when compared to conventional diesel fuel.

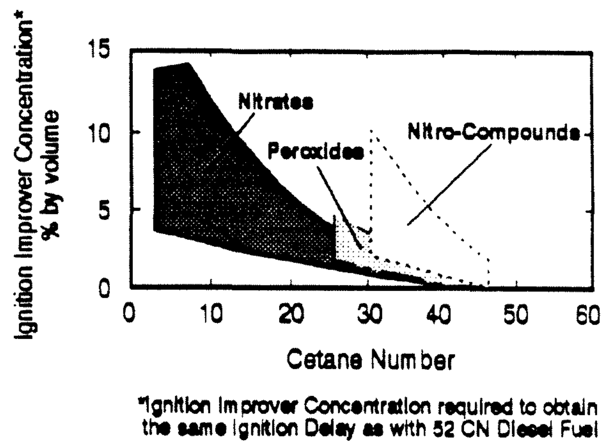

Figure 8-1., Ignition improver additives.

Of the commercial ignition improvers for alcohols, Avocet™ manufactured by ICI America, Inc. is one of the most popular and most widely tested. Avocet™ has a proprietary composition, but is known to contain a lubricant and corrosion inhibitor in addition to the active ignition improving compounds, which are nitrate esters; these components are diluted in methanol. The lubricant and corrosion inhibitor are present to protect the precise components of the diesel fuel injection systems, serving the same function as additives used to protect gasoline carburetor and fuel injection systems. Avocet™ is prepared in various concentrations by blending with chemical - grade neat methanol. The characteristics of Avocet™ are described below:

Appearance: Clear pale yellow liquid
Specific Gravity: 1.15
% Volatile by Volume: 25
Ingredients: Nitrate Ester and Methanol

The values used for methanol and Avocet™ in calculating the inputs for the emissions and carbon balance fuel consumption calculations are as follows:

	Methanol	Avocet™*
Specific Gravity	0.794	1.15
% Carbon by Wt.	37.5	35
% Hydrogen by Wt.	12.6	7
% Oxygen by Wt.	49.9	50
% Nitrogen by Wt.	--	8
Molecular Wt.	32.04	--

*Values provided by ICI America, Inc.

Avocet™ was recently used in a study to determine the performance and emissions of a Detroit Diesel Corporation 8V-71 transit bus engine operated on methanol. [5] The minimum amount of Avocet™ which enables the methanol fuel to have similar combustion characteristics to the baseline diesel fuel was 7.5%. Because methanol burns without smoke at relatively high fuel-to-air ratios, the engine could produce higher levels of power than when using the baseline diesel fuel. The combustion efficiency of this engine using ignition-improved methanol was essentially the same as when using the baseline diesel fuel. Gaseous emissions were essentially unchanged while total particulates were reduced for this engine using ignition-improved methanol relative to the baseline diesel fuel.

Miscibility with Water and Hydrocarbon Fuels

Policy Issue #2

> Miscible refers to the capacity of mixing fluids in any ratio without separation. Ethanol and methanol are completely miscible with water, but show very poor miscibility with gasoline/diesel fuels containing traces of water. As discussed earlier in Section 5, blending of gasoline or diesel with methanol/ethanol in the presence of water may lead to a phase separation problem.

This problem can be effectively controlled by the use of additives such as higher alcohols (C_2 - C_{12}), various commercial nonionic surfactants and various anionic fatty acids surfactants. Among them, **iso-propanol, 1-butanol, n-decanol and palmitic acid** have been the most often suggested. [6]

Electric Conductivity and Oxygen Content

Policy Issue #3

> The comparatively high electrical conductivity and high oxygen content of fuel alcohols can contribute to corrosion and wear problems as well as chemical degradation of materials in a vehicle's fuel system. Solving this problem requires the selection of alcohol compatible material for the fuel system. The use of corrosion inhibitors is also a good alternative.

The addition of higher alcohols, (such as 1-butanol or n-decanol) as cosolvants not only prevents the phase separation noted earlier but also inhibits the corrosion of water-sensitive materials such as aluminum. Other additives that have been demonstrated corrosion-inhibiting characteristics are calcium sulfonate, zinc dialkyl dithiophosphate, and Proal.™

Viscosity

Policy Issue #4

> Viscosity is a measure of the resistance of a liquid to flow. The "viscosity index" is a measure of the constancy of the viscosity of a lubricant with changes in temperature, with higher values indicating viscosities that change little with temperature. The low viscosity of ethanol and methanol fuels suggests that lubrication problems with conventional fuel injection systems may be expected, especially in a diesel fuel engine. The use of higher alcohols as additives offers a better lubricity.

Cold Weather Startability

Policy Issue #5

> Ethanol- and methanol-fueled spark ignition (SI) engines have proven difficult to start at ambient temperatures below approximately 10°C (50°F). This problem can be solved by mixing some additives for cold start improvement.

The cold startability of methanol and ethanol fuels improve greatly when a small amount of more volatile fuels such as **gasoline** is mixed in the alcohol. [7]

The use of **dimethyl ether (DME)** has been proposed to improve the cold starting performance of methanol-fueled SI engines. [8] DME could be generated on-board through catalytic dehydration of methanol, which is an exothermic reaction described by the following equation:

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O + \text{Heat}$$

DME has a high vapor pressure, between that of propane and butane, (as shown in Figure 8-2 [9]). It also has wide flammability limits, 3.4 - 18.0 vol %, and is therefore capable of promoting engine cold starting to below -30°C (-22°F).

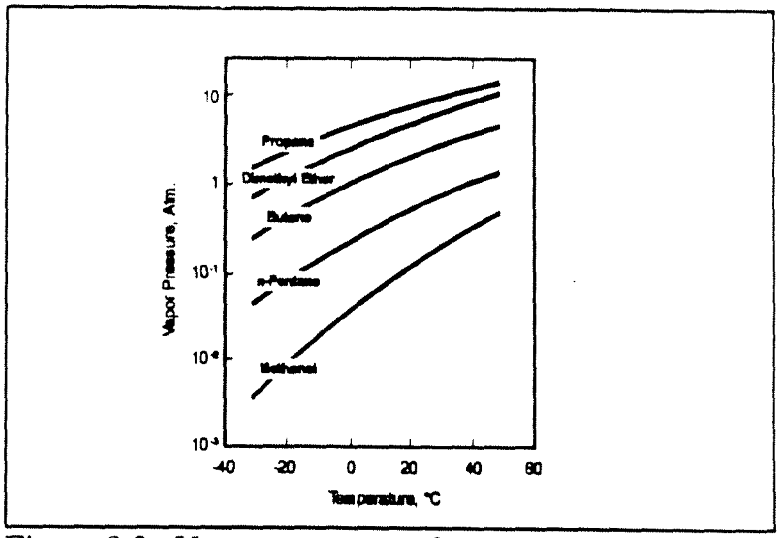

Figure 8-2., Vapor pressures of several fuels.

Conclusion

As a general rule, the fuel properties of methanol and ethanol can be significantly improved by the addition of higher alcohols. Higher alcohols offer the advantage of higher calorific value and better lubricity. In general, increasing the carbon content in the alcohol molecule improves the self-ignition properties of the higher alcohols. In addition, mixtures of methanol and higher alcohols also improve the widespread applicability of alcohol engine concepts, due to reduced wear and lube oil-related problems. Advanced methanol production processes, currently under development, may choose to produce a "fuel-grade" methanol with a lower selectivity, thus resulting in a methanol formula containing a considerable amount of higher alcohols (up to 30%, from propanol to duodecanol). [10]

ENDNOTES:

1. Nichols, Roberta J., "Applications of Alternative Fuels." SAE Paper 821573.

2. Rogers, G. W., et al., "Influence of the Methanol Fuel Composition on Performance and Exhaust Emissions of Diesel-Derived Alcohol Engines." SAE Paper 881197.

3. Ibid.

4. *Oxy-Fuels News*, April 23, 1990, p. 5.

5. Urban, Charles M., et al., "Performance and Emissions of a DDC 8V-71 Engine Fueled with Cetane Improved Methanol." SAE Paper 892064.

6. Tshiteya, Rene M., et al., "The Impact of Phase Separation in Alcohol/Gasoline Blends on the Existing Fuel Distribution System." Paper accepted for publication and presentation at the 25th Intersociety Energy Conversion Engineering Conference in Reno, Nevada, August 12-17, 1990.

7. Iwai, Nobuo et al., "A Study of Cold Startability and Mixture Formation of High-Percentage Methanol Blends." SAE Paper 880044.

8. Kozole, Karl H. and James S. Wallace, "The Use of Dimethyl Ether as a Starting Aid for Methanol-Fueled SI Engines at Low Temperatures." SAE Paper 881677, 1988.

9. Karpuk, Michael E., and Scott W. Cowley, "On Board Dimethyl Ether Generation to Assist Methanol Engine Cold Starting." SAE Paper 881678, 1988.

10. Hohlein, B., et al., "Synthesis Gas Production and Synthesis of Energy Alcohol." 7th ISAFT, Paris, France, 1986.